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Ring-opening Polymerization of 2-Oxabicyclo[2.2.2]octan-3-one and the Influence of Stereochemistry on the Thermal Properties of the Polyesters

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Electronic Supplementary Information

Abstract Polyesters with cyclic structures in the main chain typically possess superior mechanical and thermal properties together with chemical recyclability. Ring-opening polymerization (ROP) of bridged or fused bicyclic lactones is a simple, and in most cases controlled method to synthesize polyesters with alicyclic moieties in the polymer backbone. The stereochemistry of the alicyclic structures has a great effect on the polymer properties, which can be regulated by varying the polymerization conditions. Here, we report a systematic investigation on the ROP of 2-oxabicyclo[2.2.2]octan-3-one (**[2.2.2]VL**) under different conditions. When initiated by *n*-butyl lithium (*n*-BuLi) or catalyzed by trifluoromethanesulfonic acid (TfOH) in the presence of benzyl alcohol, **P[2.2.2]VLs** containing all *cis*-1,4 disubstituted cyclohexane ring were obtained. However, **P[2.2.2]VLs** initiated by sodium methoxide (MeONa) or catalyzed by organic superbase contained both *cis* and *trans* isomeric structural units. The *cis* to *trans* transformation mechanism under these conditions was manifested, and the effect of stereochemical variations on the properties of **P[2.2.2]VL** was revealed. The stereoregular **P[2.2.2]VLs**, both *cis* and *trans*, exhibited higher crystallinity and melting temperatures (T_m) than those of the stereoirregular isomers. Finally, the degradation of **P[2.2.2]VL** with acid at high temperature could recover 3-cyclohexenecarboxylic acid.

Keywords 2-Oxabicyclo[2.2.2]octan-3-one; Ring-opening polymerization; Stereochemistry; Polyester; Thermal properties

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INTRODUCTION

Ring-opening polymerization (ROP) of cyclic monomers is an important method for the preparation of various functional polymers.[1] ROP of lactones and lactides is the most widely used method to prepare polyesters, which have widespread applications as biodegradable materials and potentially closed-loop recyclable plastics. Developments in metal catalysts as well as organic catalysts have greatly advanced this field, enabling the easy access to a range of well-defined polyesters with controlled molar mass, end groups, low dispersities, stereochemistry, and topology.[2−16]

Bicyclic monomers can undergo ROP to afford polymers with ring structures in the main chain. The polymerization behavior of these monomers is closely related to the ring size and bridge atoms as demonstrated by early works of Hall and Okada.[17−19] Incorporation of cylic structurers into polymer backbone can improve the thermal and mechanical properties. In addition, stereochemical configuration associated with the ring structure (*cis* or *trans*) is another factor to further regulate the polymer properties.[20−23] For example, Chen *et al.*[24,25] synthesized poly(γ-butyrolactone) containing *trans*-1,2 disubstituted cyclohexane through the ROP of cyclohexane *trans*-cyclohexane-fused γ-butyrolactones. Other groups also reported alicyclic polyesters, polycarbonate, polyphosophoesters, and polyurethanes *via* the ROP of corresponding ring-fused bicyclic monomers.[26−31] Bridged bicyclic lactones are another type of bicyclic monomers that undergo ROP and generate (semi)crystalline polyesters with melting temperatures (T_m) around 230 °C[17,32−34] (Scheme 1, **I**–**III**). The lactones containing one oxygen heteroatom (Scheme 1, **IV**/**VI**) can undergo cationic ring-opening polymerization (cROP) to obtain polyesters with T_m of about 150 °C.[18,35] The polyester from monomer **V** has high crystallinity, low molar mass due to the poor solubility.[36] Very recently, we developed a hybrid monomer strategy, and designed a [3.2.1]bicyclic lactone (**III**), which exhibits both high polymerizability and depolymerizability. The resulting polyester can not only

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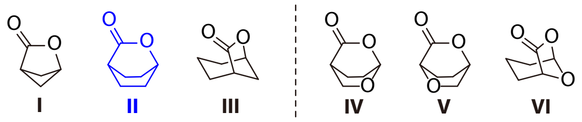


Scheme 1 Bridged bicyclic lactones studied in ROP.

be quantitatively recovered to monomers in hot solution, but also enhance thermal and mechanical properties compared with polycaprolactone.[37] 2-Oxabicyclo[2.2.2]octan-3-one (**[2.2.2]VL**, **II**) is one of the commercially available bridged bicyclic lactones, which can be easily obtained from 4-hydroxy benzoic acid.[38] The anionic polymerization of **[2.2.2]VL** has been investigated by several groups.[17,33,34] Hall *et al*. first studied the ROP of **[2.2.2]VL** with sodium at 150 °C, and got a polymer with a T_m of 195 °C, but they did not fully characterize the polymer.[17] Ceccarelli *et al*. investigated the anionic ROP of **[2.2.2]VL**, they got an all *cis* polymer with *n*-BuLi, and a mixture of *cis* and *trans* polymer with sodium *tert*-butoxide. The *cis/trans* configuration of the polymer was analyzed by NMR, and the polymerization mechanism was incorrectly interpreted.[33] Herein, the ROPs of **[2.2.2]VL** under different conditions were systematically investigated, aiming at clarifying the polymerization mechanism, regulating the stereochemistry of the polymers, and elucidating the effect of stereochemistry on the polymer properties. Finally, the degradation of **P[2.2.2]VL** with acid at high temperature and recovery of monomers were attempted. It is believed that these results can lay a foundation for further study of bridged lactones from renewable resources and preparation of high performance polyesters with closed-loop recycling.

EXPERIMENTAL

Materials

2-Oxabicyclo[2.2.2]octan-3-one (**[2.2.2]VL**, TCI Co.) was recrystallized from a mixture of dry ethyl acetate and cyclohexane twice, dried at 40 °C under vacuum for 12 h, and stored under nitrogen atmosphere. It is a white crystal with a T_m of 85 °C. Cyclic triphosphazene base (CTPB) was a kind gift from Prof. Zhibo Li, which was synthesized according to a previous report.[39] All other chemicals were purchased from commercial sources and used as received.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX 400 spectrometer (^{1}H: 400 MHz) using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Matrix-assisted laser desorption/Ionization time of flight mass spectrometry (MALDI-TOF-MS): an AB-Sciex 5800 instrument was used in reflection mode. Dihydroxybenzene (DHB) was used as a matrix. Polymers and DHB were each dissolved in THF, combined in a *ca*. 1:2000 mass ratio of polymer to matrix, and applied to the target plate. Decomposition onset temperatures (T_d, defined at 5% weight loss) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q600 TGA Thermogravimetric Analyzer, TA Instrument. Differential scanning calorimetry (DSC) was performed on a Q2000 TA Instruments. Samples were heated from room temperature to 300 °C at a rate of 10 °C/min under a nitrogen purge and held for 2 min to erase the thermal history. They were then cooled to −60 °C at a rate of 10 °C/min and held for another 2 min. The second heating scan from −60 °C to 300 °C was then recorded. The glass transition temperatures (T_g) reported are taken from the second cycle.

Polymer Synthesis

Unless otherwise noted, all the ROPs of **[2.2.2]VL** were carried out in a nitrogen atmosphere glove box.

CTPB-catalyzed ROP of [2.2.2]VL

A toluene solution of CTPB (0.01 equiv.) and benzyl alcohol (BnOH, 2.16 mg, 0.01 equiv.) were mixed in a vial for 10 min. This mixture was then transferred to a 10 mL Schlenk containing **[2.2.2]VL** (252 mg, 2 mmol, 1 mol/L) in 2 mL of toluene. The polymerization was carried out at 30 °C for 8 h, and the solution gradually gelated with time. Then, dichloromethane (DCM) was added to dissolve the polymer, and after precipitation into methanol for three times, **P[2.2.2]VL** was obtained and dried overnight in a vacuum oven at 50 °C with a yield of 78%.

For the synthesis of acetyl-end capped **P[2.2.2]VL** (**Acet-P[2.2.2]VL**), acetyl chloride and pyridine (0.05 equiv.) were added after 3 h, and the polymer was recovered, purified and dried under similar conditions.

MeONa-initiated ROP of [2.2.2]VL

[2.2.2]VL (252 mg, 2 mmol) and MeONa (2.16 mg, 0.02 equiv.) were dissolved in DMF. The solution was stirred at 30 °C for 12 h before adding benzoic acid to quench the reaction. After usual workup, the polymer was obtained in 83% yield.

n-BuLi-initiated ROP of [2.2.2]VL

[2.2.2]VL (504 mg, 4 mmol) and 2 mL of toluene were added to a 10 mL flame-dried Schlenk flask interfaced to the dual-manifold Schlenk line and then 0.8 mol% of *n*-BuLi was injected. After 3 h, the polymerization was quenched by adding 0.5 mL of MeOH. The obtained polymer was dissolved in DCM and precipitated in methanol for three times. The polymers were dried overnight in a vacuum oven at 50 °C with a yield of 89%.

TfOH-catalyzed ROP of [2.2.2]VL

In a typical polymerization process, **[2.2.2]VL** (252 mg, 2 mmol) and BnOH (10.8 mg, 0.05 equiv.) were dissolved in 1 mL of desired solvent. The polymerization was initiated by rapid addition of TfOH *via* a syringe. The reactor was sealed, immersed in an oil bath thermostated at 60 °C. The reaction was monitored by ^{1}H-NMR at intervals. When the monomer conversion ceased to increase, the polymerization was quenched with triethylamine. The obtained polymer was dissolved in DCM, precipitated in methanol for three times. The polymers were dried overnight in a vacuum oven at 50 °C with a yield of 81%.

Condensation Polymerization of *Trans*-4-hydroxycyclohexanecarboxylic Acid[40]

Trans-4-hydroxycyclohexanecarboxylic acid (2.88 g, 20 mmol) and DPTS (11.3 g, 40 mmol, 2 equiv.) prepared in advance from 4-dimethylaminopyridine and *p*-toluenesulfonic acid were added to a reactor attached to the Schlenk line. *N,N'*-diisopropylcarbodiimide (3.27 g, 26 mmol, 1.3 equiv.) dissolved in DCM was added to the reactor *via* a springe. After being stirred at 25 °C for 12 h, the mixture was poured into methanol to precipitate the polymer. The obtained polymer was dissolved in DCM, precipitated in methanol for another twice. The polymers were dried overnight in a vacuum oven at 50 °C with a yield of 68%.

Chemical Recyclability of P[2.2.2]VL

P[2.2.2]VL (800 mg) and TfOH (0.05 mL) were added consequently into a 10 mL Schlenk tube filled with toluene. The mixture was stirred under 120 °C for 24 h. ^{1}H-NMR spectra revealed that 50 % of **P[2.2.2]VL** has been degraded. After the degradation products being washed with NaCl solution, 3-cyclohexenecarboxylic acid was recovered in 40% yield *via* distillation under 100 Pa at 80–90 °C.

RESULTS AND DISCUSSION

ROP of [2.2.2]VL

Monomer **[2.2.2]VL** can be regarded as a simple coupling of two δ-valerolactone (δ-VL). The ROP of δ-VL has been achieved with a variety of organocatalysts, such as *N*-heterocyclic carbene,[41,42] 4-(dimethylamino)pyridine,[43] thiourea/amine,[44] guanidine,[45] phosphazene,[46] trifluoromethanesulfonic acid (TfOH), methanesulfonic acid, and diphenyl phosphate (DPP),[47,48] PVL is a semicrystalline polymer (T_g=−55 °C, T_m=58 °C). The substituted δ-VLs can also undergo ROP utilizing the above catalysts to obtain functional degradable polyesters.[49] We screened several catalysts for the ROP of **[2.2.2]VL** to obtain **P[2.2.2]VL** with different stereochemistry. The TBD and DBU-catalyzed ROP of **[2.2.2]VL** in DCM with BnOH as initiators was first tested, no polymerization occurred even with high loading of catalysts and in a long time. Changing to a cyclic phosphazene superbase, CTPB, which has been demonstrated effective for the ROP of γ-BL[39] and ε-CL,[50] did promote the ROP of **[2.2.2]VL**, suggesting that **[2.2.2]VL** is less polymerizable than VL. The ROP of **[2.2.2]VL** was then investigated in more detail at 30 °C in DCM with CTPB as the catalyst (Table 1). Increasing the monomer to initiator ratio led to the increase of polymer molar mass, but the monomer conversion became low due to gelation of the reaction mixture. Polymers were recovered in 61%–88% yields (Table 1 and Fig. S1 in the electronic supplementary information, ESI).

Table 1 Results of ROP of **[2.2.2]VL** catalyzed by CTPB. ^{a}

Entry	$[M]_0$:[I]:[C]	Conv. ^{b} (%)	Yield ^{c} (%)	M_n ^{d} (kDa)
1	50:1:1	95	88	6.1
2	100:1:1	88	78	10.1
3	200:1:2	85	73	12.6
4	400:1:4	72	61	14.9

^{a} M_0=1 mol/L, toluene, 30 °C, 8 h; ^{b} Determined by ^{1}H-NMR; ^{c} Determined by gravimetric method; ^{d} Determined by comparing the integration ratio of —CH— peak signal (δ=2.26 ppm) to —CH_2— (δ=5.12 ppm) in ^{1}H-NMR spectrum of **P[2.2.2]VL**.

The obtained **P[2.2.2]VL** is insoluble in common solvents like tetrahydrofuran (THF), ethyl acetate, DMF and DMSO, limiting the measurement of its molar mass by SEC. The ^{1}H-NMR spectra of a low molar mass **P[2.2.2]VL** (Table 1, entry 1) before and after being end-capped with acetyl group are shown in Fig. 1, where peaks a, b, c are the proton signals of the cyclohexane units, and their ratio is consistent with 1/4/1. The proton signals of the terminal methylene groups (—CH_2OH) are assigned to peaks f and f' (δ=3.61, 3.89 ppm), which disappeared after being end-capped with acetyl chloride, confirming the BnOH-initiated linear polymer structure and complete end-capping. This linear structure of **P[2.2.2]VL** was further confirmed by the MALDI-TOF-MS spectra (Figs. 1B and 1D). By comparing the integration ratio of peak a (2.26 ppm) and d (5.12 ppm) in the ^{1}H-NMR spectra of the polymers, the M_n of the polymers can be calculated (Table 1).

Next, we used MeONa to initiate the anionic ROP of

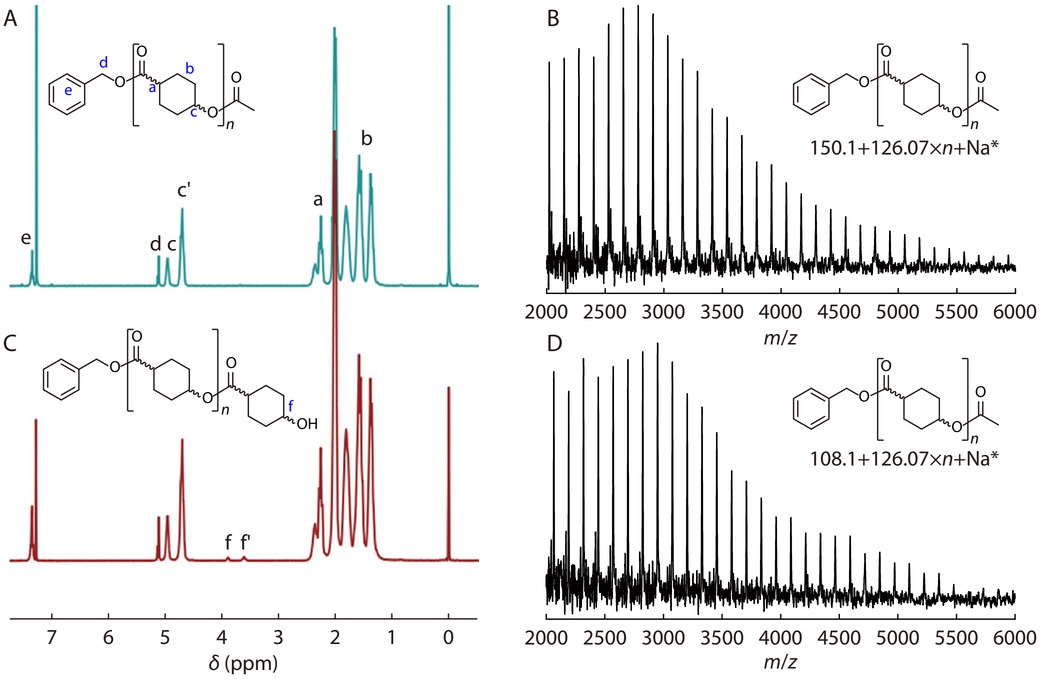


Fig. 1 (A) ^{1}H-NMR and (B) MALDI-TOF-MS spectra of **P[2.2.2]VL** after being end-capped; (C) ^{1}H-NMR and (D) MALDI-TOF-MS spectra of **P[2.2.2]** (Table 1, entry 1).

[2.2.2]VL in DMF, both of the ^{1}H- and ^{13}C-NMR spectra of **P[2.2.2]VL** are essentially similar to those of **P[2.2.2]VL** catalyzed by CTPB (Figs. S2 and S3 in ESI). However, the MALDI-TOF-MS spectrum (Fig. 2A) revealed that **P[2.2.2]VL** contains cyclic polymers, indicative of intramolecular transesterification *via* backbiting.[51] *n*-BuLi could also initiated the anionic ROP of **[2.2.2]VL** in toluene as reported in previous work.[33] Both NMR (Figs. S4 and S5 in ESI) and the MALDI-TOF-MS (Fig. 2B) spectra confirmed the formation of a low molar mass linear **P[2.2.2]VL** (M_n=2.1 kDa) with no cyclic oligomer contamination.

The ROP of **[2.2.2]VL** was further performed using strong acid TfOH as a catalyst and BnOH as an initiator in different solvents, temperature, and monomer to initiator ratio (Table 2). The ROPs are generally slow and the polymer yields are also low even after long time. The ROP in chlorobenzene (PhCl) at 20 °C gave 21% polymer after 2 days. ^{1}H-NMR and MALDI-TOF-MS spectra of the obtained polymer confirmed the formation of linear **P[2.2.2]VL** initiated by BnOH (Fig. 3). At low [M]/[I] ratio, increasing the reaction temperature from 20 °C to 60 °C can increase the monomer conversion (Table 2, entries 1 and 2). But at a higher [M]/[I] ratio, the final monomer conversion was even lower at 60 °C (Table 2, entries 2–4). ^{1}H-NMR and MALDI-TOF-MS spectra of **P[2.2.2]VL** obtained at 60 °C revealed the existence of cyclohexene moieties at the polymer chain ends (g, δ=5.68 ppm), indicating that elimination reaction occurred during the ROP at 60 °C (Fig. 3). These elimination side reactions also account for the low monomer conversion at 60 °C. In the absence of BnOH (Table 2, entry 5), little polymer was obtained even after 2 days at 60 °C, confirming that alcohol initiator was necessary to initiate the ROP (Fig. S6 in ESI). The ROP of **[2.2.2]VL** at 20 °C in DCM and chloroform for 8 days gave similar results as that in PhCl (Table 2, entries 6–9).

Collectively, the ROP of **[2.2.2]VL** can be fulfilled by both anionic and cationic mechanisms, the CTPB-catalyzed ROP can reach high monomer conversion and high molar mass of polymers, but the TfOH-catalyzed ROP is slow with side reactions. Due to the low solubility of **P[2.2.2]VL** in toluene, only low molar mass polymer can be obtained in the anionic ROP initiated by *n*-BuLi.

Stereochemistry of P[2.2.2]VL

According to the general ROP mechanism of lactones, the ROP of **[2.2.2]VL** will result in the formation of a conformationally locked 1,4-*cis* disubstituted cyclohexane linkage in the polymer main chain. But close comparison of the ^{1}H-NMR spectra of **P[2.2.2]VL** catalyzed by CTPB and TfOH (Fig. 4) indicated that this is not the case for **P[2.2.2]VL** obtained by CTPB. The ^{1}H-NMR spectrum of the TfOH-catalyzed sample is simple and in accordance with the expected *cis* configuration structure.[33] However, the ^{1}H-NMR spectrum of the CTPB-catalyzed **P[2.2.2]VL** is complicated, implying the existence of *trans* stereoisomers.

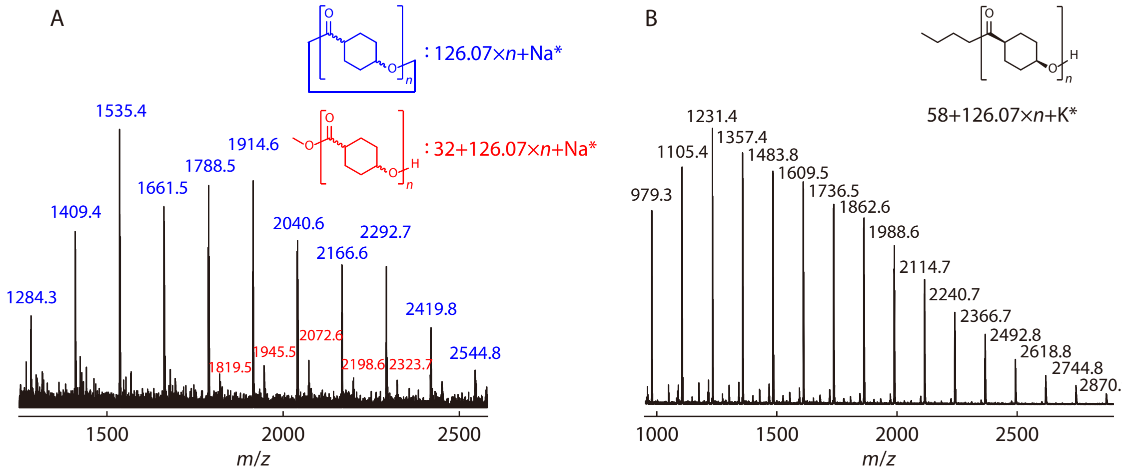


Fig. 2 MALDI-TOF-MS spectra of **P[2.2.2]VL**: (A) initiated by MeONa; (B) initiated by *n*-BuLi.

Table 2 TfOH-catalyzed ROP of **[2.2.2]VL**.

Entry	Solvent	$[M]_0$:[I]:[C]	$[M]_0$ (mol/L)	Temp. (°C)	Time (day)	Conv. [a] (%)	Yield [b] (%)
1	PhCl	20:1:0.1	2	20	2	35	21
2	PhCl	20:1:0.1	2	60	1	88	81
3	PhCl	50:1:0.1	2	60	2	44	36
4	PhCl	100:1:0.1	2	60	2	26	13
5	PhCl	20:0:0.1	2	60	2	10	–[c]
6	$CHCl_3$	20:1:0.1	1	20	8	29	24
7	CH_2Cl_2	20:1:0.1	1	20	8	43	35
8	$CHCl_3$	50:1:0.1	5	20	8	30	28
9	CH_2Cl_2	50:1:0.1	5	20	8	26	23

[a] Determined by ^{1}H-NMR; [b] Determined by gravimetric method; [c] No polymer formation.

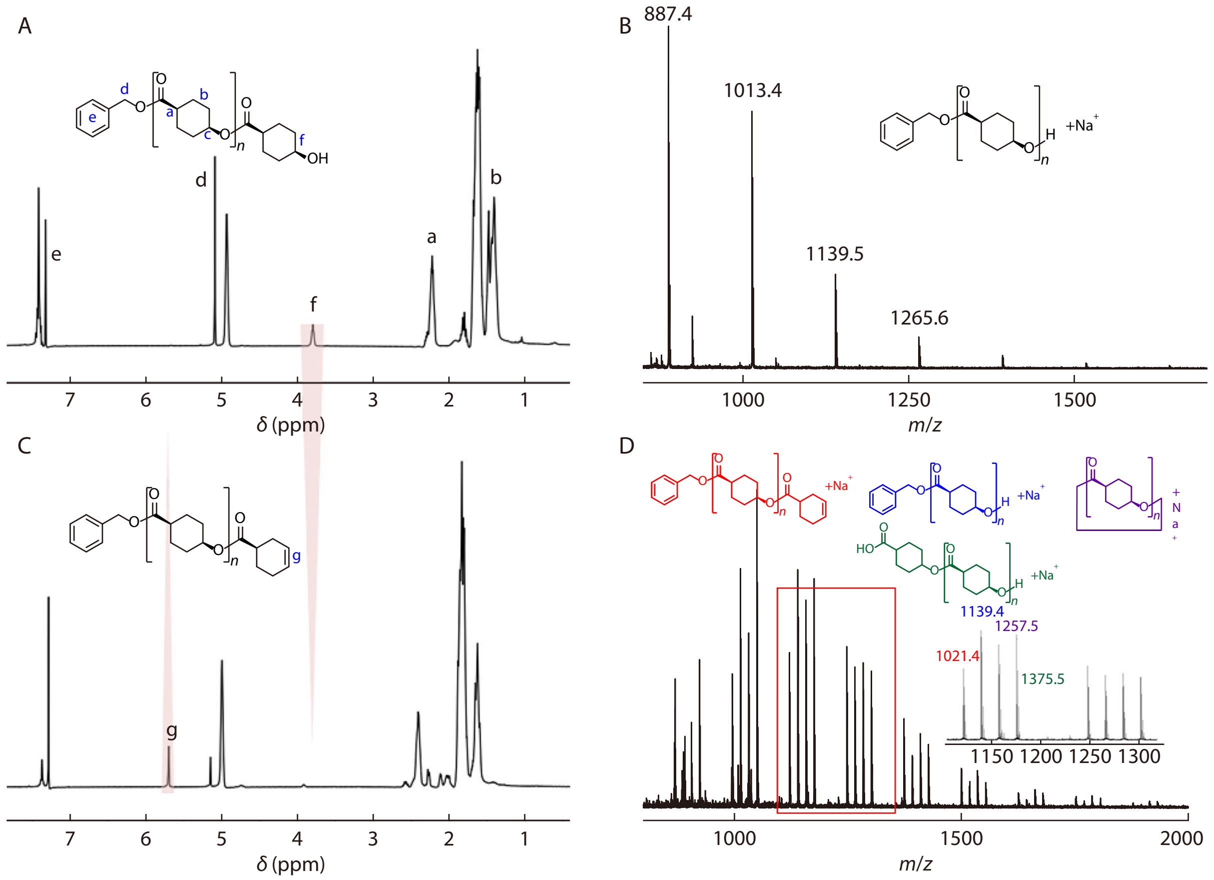


Fig. 3 (A and C) ^{1}H-NMR and (B and D) MALDI-TOF-MS spectra of **P[2.2.2]VL** catalyzed by TfOH: (A and B) polymerized at 20 °C; (C and D) polymerized at 60 °C.

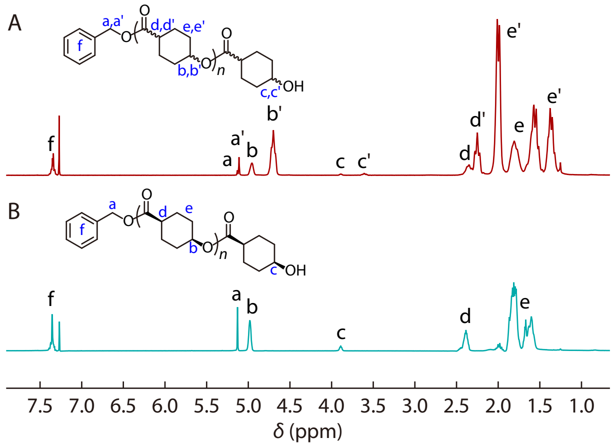


Fig. 4 ^{1}H-NMR spectra of **P[2.2.2]VL** catalyzed by (A) CTPB (Table 1, entry 1); (B) TfOH (Table 2, entry 1).

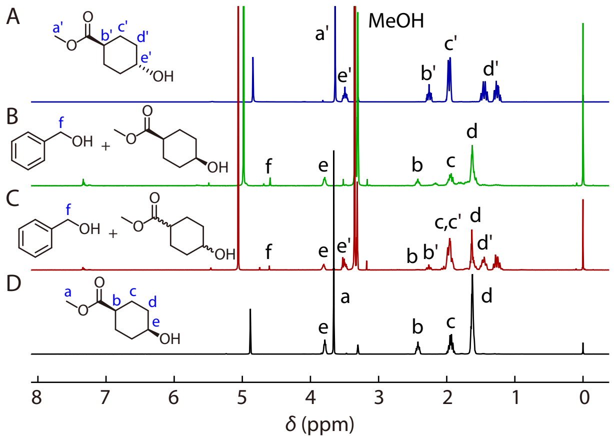


Fig. 5 ^{1}H-NMR spectra of the methanolytic products of **P[2.2.2]VL** and the pure *cis* and *trans* compounds. (A) *trans*-methyl 4-hydroxycyclohexanecarboxylate; (B) TfOH-catalyzed **P[2.2.2]VL**; (C) CTPB-catalyzed **P[2.2.2]**; (D) *cis*-methyl 4-hydroxycyclohexanecarboxylate.

To confirm the existence of both *cis/trans* isomeric structures, these two polymer samples were dissolved in $CDCl_3$/MeOD, and a catalytic amount of MeONa was added, the mixture was incubated at 35 °C overnight. ^{1}H-NMR spectra of the solutions were then measured (Fig. 5). Clearly, the TfOH-catalyzed **P[2.2.2]VL** gave pure *cis* monomer, *cis*-methyl 4-hydroxy cyclohexanecarboxylate, while the CTPB-catalyzed **P[2.2.2]VL** gave a mixture of *cis* (b, c, d, e) and *trans* isomers (b′, c′, d′, e′). By integrating the corresponding peaks (Fig. 5, b and b′), the ratio of *cis* and *trans* isomers in the stereoirregular **P[2.2.2]VL** can be determined. The results are summarized in Table 3. When CTPB is used as catalyst, the *trans* isomer is always dominant (Table 3, entries 1–3), but the

Table 3 Proportion of *cis/trans* isomers and the thermal data of **P[2.2.2]VL**.

Entry	Catalyst	$[M]_0$:[I]	*cis*:*trans* [a]	T_m [b] (°C)	T_c [b] (°C)
1	CTPB	100:1	27:73	240	190
2	CTPB	200:1	30:70	238	190
3	CTPB	400:1	34:66	235	192
4	MeONa	50:1	42:58	233	173
5	*n*-BuLi	125:1	100:0	245	215
6	TfOH	20:1	100:0	242	212
7	TfOH	50:1	100:0	244	224

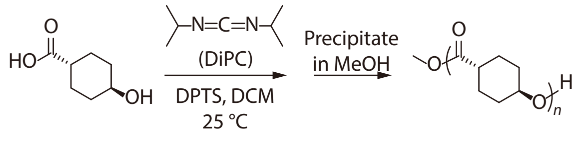
[a] Calculated from the integration of the *cis* (δ=4.97 ppm) / *trans* (δ=4.69 ppm) peaks (Fig. 4); [b] Determined by DSC.

ratio of *cis/trans* isomers increases with increasing the monomer to initiator ratio. Besides, the *n*-BuLi-initiated polymer keeps the *cis* configuration as in the previous report,[33] while the MeONa-initiated polymer also gave a *cis* and *trans* isomer mixture as in the case of CTPB system.

Effect of Stereochemistry on the Thermal Properties of P[2.2.2]VL

The *cis/trans* ratio in **P[2.2.2]VL** affects its thermal properties. Nevertheless, these polymers are all semicrystalline polymers with variable T_m and T_c. No glass transition temperature (T_g) could be detected, owing to the rigidity of the polymer backbones. The T_m of the CTPB-catalyzed **P[2.2.2]VL** varied from 235 °C to 240 °C with T_c around 190 °C (Fig. S9 in ESI, Table 3, entries 1−3). The T_m of **P[2.2.2]VL** initiated by MeONa was 233 °C, with T_c around 173 °C (Table 3, entry 4). This may be due to the low molar mass of the polymer and the cyclic oligomer contamination. T_m tended to increase with the decrease of the *cis/trans* ratio in **P[2.2.2]VL**. This trend was owing to the existence of *cis* configuration which hinders the packing of polymer chains towards ordered crystals, thus both T_m and T_c decreased with the increase of *cis* configuration ratio. These results are consistent with previous reports on polyesters containing 1,4-disubstituted cyclohexane rings.[52−55] The T_m of **P[2.2.2]VL** initiated by *n*-BuLi reached 245 °C (Table 3, Entry 5), which was significantly higher than that of the stereoirregular **P[2.2.2]VL**. The TfOH-catalyzed **P[2.2.2]VL** shows similar T_m and T_c (Fig. S10 in ESI), indicating that the all *cis*-**P[2.2.2]VL** also have better regularity than the stereoirregular **P[2.2.2]VL**. Since the CTPB-catalyzed **P[2.2.2]VL** has higher molar mass than that of the TfOH-catalyzed **P[2.2.2]VL**, the 5% weight loss temperature was about 10 °C higher (Figs. S9 and S10 in ESI).

To reveal the relationship between the stereochemistry and the properties of **P[2.2.2]VL**, the polymer with full *trans* configuration was synthesized by polycondensation of *trans*-4-hydroxycyclohexanecarboxylic acid (Scheme 2). The ^{1}H-NMR spectrum and DSC thermograms of this *trans*-**P[2.2.2]VL** are shown in Fig. 6. The second-heating DSC thermograms of **P[2.2.2]VL** with different stereochemistry are stacked in Fig. 7. It is clear that *trans*-**P[2.2.2]VL** shows the highest T_m of 252 °C, followed by *cis*-**P[2.2.2]VL** (TfOH: 244 °C, *n*-BuLi: 245 °C).



Scheme 2 Synthesis of all *trans* **P[2.2.2]VL** by polycondensation.

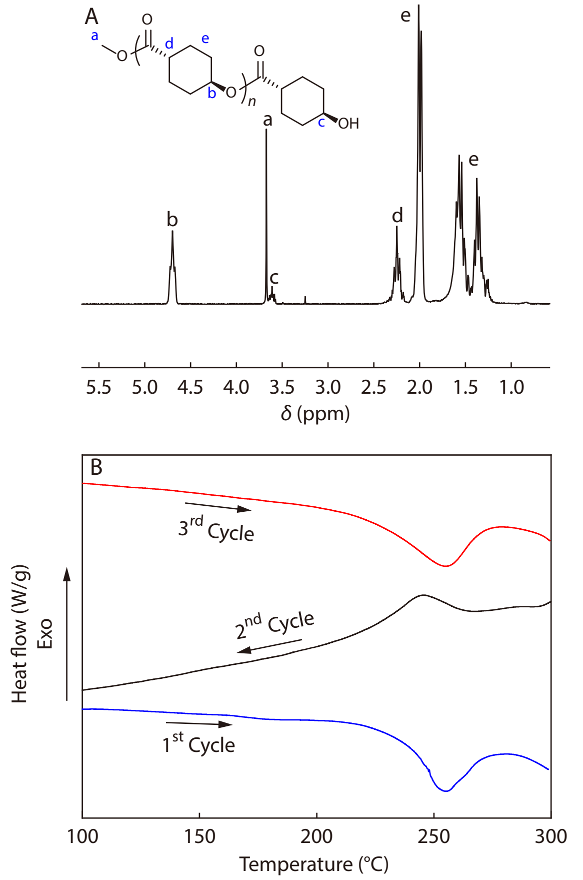


Fig. 6 (A) ^{1}H-NMR spectrum; (B) DSC thermograms of *trans* **P[2.2.2]VL**.

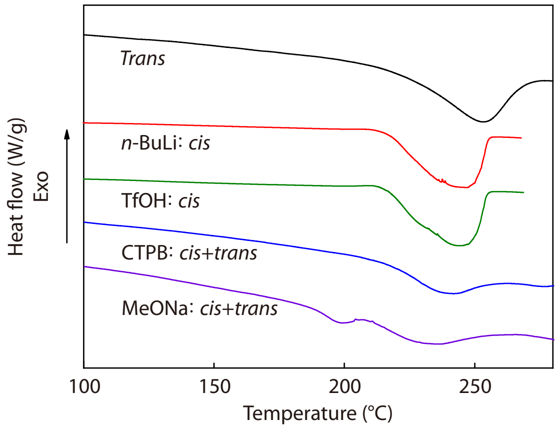
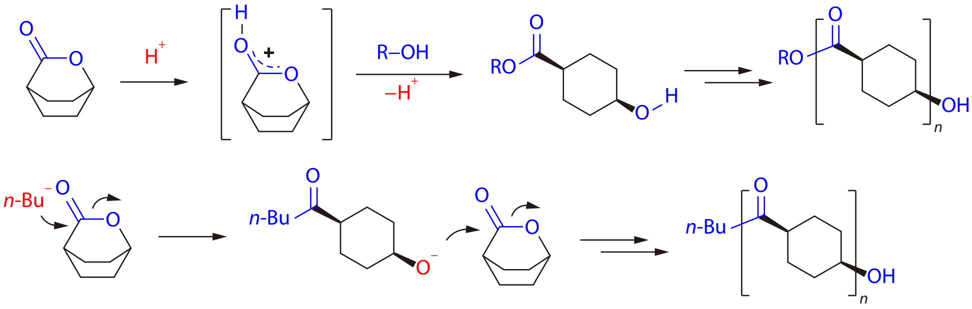
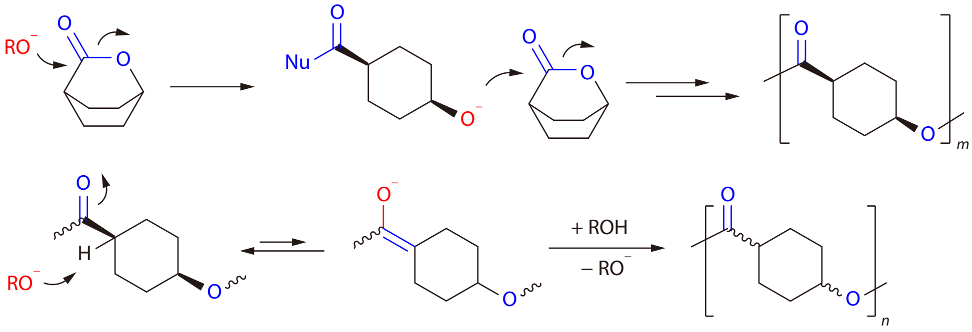


Fig. 7 The second heating DSC thermograms of **P[2.2.2]VL**s with variable stereochemistry (CTPB: *cis*:*trans*=27:73; MeONa: *cis*:*trans*=42:58).

The stereoirregular **P[2.2.2]VLs** with different *cis/trans* ratios show the lowest T_m (CTPB: 240 °C, MeONa: 233 °C), and their melting and crystallization peaks are relatively low, indicative of low crystallinities of the stereoirregular **P[2.2.2]VLs**. This was interpreted that the *trans* 1,4-disubstituted cyclohexane configuration is more extended and can effectively promote the tight accumulation of polymer segments to the stable



Scheme 3 Normal cationic and anionic ROP mechanism of **[2.2.2]VL.**



Scheme 4 Proposed mechanism of formation of stereoirregular **P[2.2.2]VL**.

crystal than the *cis* configuration.[52−55]

Mechanism of the ROP

All *cis*-**P[2.2.2]VLs** were obtained when the ROP of **[2.2.2]VL** was catalyzed by TfOH. It should be formed by the normal acyl-oxygen bond cleavage, which is consistent with the mechanism of activated monomer reported in the literature.[56] Brønsted acid acts as an electrophilic reagent; it first activates the monomer, which enhances the electrophilicity of the carbonyl carbon. Alcohols then attack the carbonyl carbon, leading to the breaking of the acyl-oxygen bond. This process is repeated to get *cis*-**P[2.2.2]VL**, as shown in Scheme 3. *n*-BuLi-initiated ROP of **[2.2.2]VL** also generated stereoregular *cis*-**P[2.2.2]** by normal anionic mechanism through acyl-oxygen bond cleavage (Scheme 3).

In the previous study,[33] stereoirregular **P[2.2.2]VL** was proposed to be formed through two different process. The *cis*-isomer was formed by normal anionic mechanism, and the *trans*-isomer was attributed to the alkoxy bond cleavage. While this latter mechanism is accepted in the ROP of β-butyrolactone derivatives,[1] it is unlikely for the ROP of **[2.2.2]VL**. Since stereoirregular PLLA and other polyesters from the ROP of corresponding chiral monomers are frequently reported,[57−60,37] we propose that the *trans*-isomer could be transformed from the originally formed *cis*-isomer. This isomerization (racemization, epimerization) can only occur in the presence of strong base through keto-enol tautomerism (Scheme 4). This process occurred immediately after the formation of *cis* units, high concentration of alkoxide anion lead to high degree of isomerization of **P[2.2.2]VL**, which is consistent with our experimental results that the proportion of *trans/cis* isomers increased with decreasing ratio of monomer to initiator (Table 3, entries 1−3). To verify this hypothesis, we performed the following experiments. The *cis*-**P[2.2.2]VL** catalyzed by TfOH was stirred in the presence of CTPB at 30 °C and the time-dependent ^{1}H-NMR spectra of the mixture was followed (Fig. 8). A group of new peaks appeared after 4 h (δ=4.70 ppm), which is consistent with the chemical shifts of the *trans* configuration unit in **P[2.2.2]VL**. It thus confirmed that the *cis*-isomer had been transformed into *trans*-isomer by strong base such as CTPB or MeONa.

Degradation of P[2.2.2]VL and Recovery of Monomer

As mentioned earlier, the TfOH-catalyzed ROP of **[2.2.2]VL** at high temperature caused severe elimination of the secondary hydroxyl group at the end of the polymer chain. So we tried the acid-catalyzed degradation of **P[2.2.2]VL** in the presence of TfOH at 120 °C for 24 h. The crude product was purified by vacuum distillation and analyzed with ^{1}H-NMR (Fig. 9). 3-Cyclohexenecarboxylic acid was recovered in 40% yield as the pure compound. The melt polymerization of this compound was carried out in bulk catalyzed by concentrated sulfuric acid at 80 °C. After 5 h, the color of the reaction medium became dark and the formed polymer was precipitated in ether and collected. The ^{1}H-NMR spectra of the obtained polymer indicated that besides **P[2.2.2]VL**, one additional new structure (1,3-disubstituted cyclohexane linkage) was formed. Because the reaction sites of double bond and carboxylic acid group were not selective, the ester bonds in the obtained polymers were located in two positions of cyclohexane (p and m) (Fig. S11 in ESI). Unfortunately, the molar mass of the polymer analyzed by SEC was only 1 kDa, owing to the relatively poor reactivities between double bonds and carboxylic acids. Intriguingly, 3-cyclohexenecarboxylic acid can be transformed directly into a new bicyclic lactone as reported in our previous study.[37]

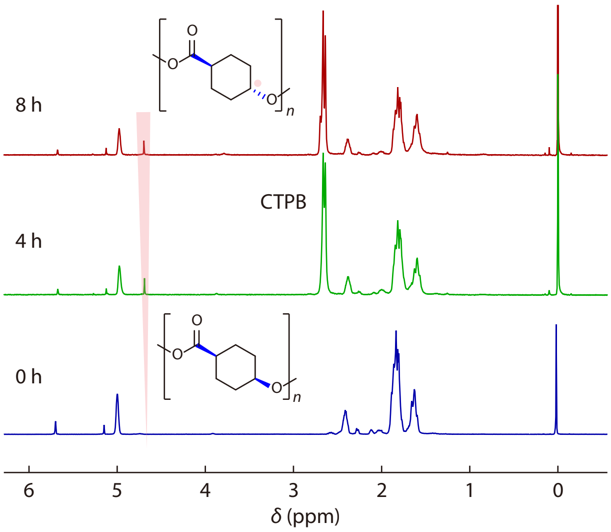


Fig. 8 ^{1}H-NMR spectra of *cis*-**P[2.2.2]VL** treated by CTPB at 30 °C.

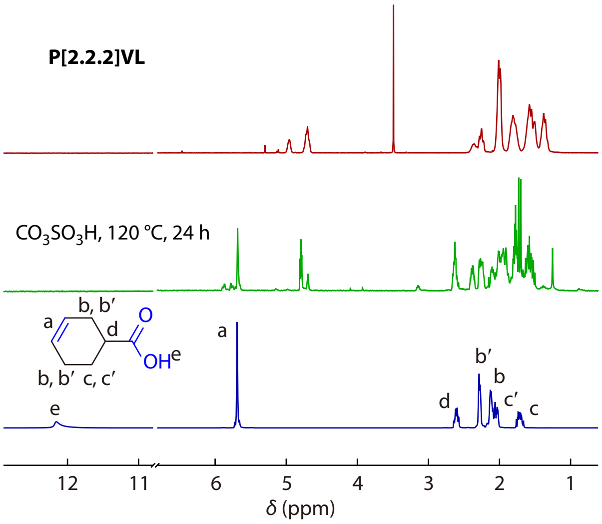


Fig. 9 ^{1}H-NMR spectra of acid-catalyzed degradation of **P[2.2.2]VL**. 3-Cyclohexenecarboxylic acid obtained by distillation.

CONCLUSIONS

The ROP of a bridged lactone **[2.2.2]VL** was systematically studied and the effect of stereochemistry on the resulting polymer properties was elucidated. The **P[2.2.2]VL** catalyzed by TfOH and initiated by *n*-BuLi were stereoregular polymers with all *cis* configuration, while **P[2.2.2]VL** catalyzed by CTPB and initiated by MeONa were stereoirregular with both *cis* and *trans* 1,4-disubstituted cyclohexane linkages. The ratio of the *cis*/*trans* isomers can be regulated by the monomer to catalysts ratios. The transformation mechanism of the *cis* to *trans*-isomers in the presence of strong base was proposed and attributed to the strong base-catalyzed epimerization of the formed *cis*-**P[2.2.2]VL**. The thermal properties of **P[2.2.2]VL** have been investigated with particular attention to the relationship between the stereochemistry of the 1,4-disubstituted cyclohexane. T_m, T_c and crystallization of *trans*-**P[2.2.2]VL** were slightly higher than those of its *cis* isomers, and they were both much higher than those of the stereoirregular **P[2.2.2]VL**. Taking advantage of the acid-catalyzed elimination of hydroxyl groups at the terminal of the polymer chains, acid-catalyzed degradation of **P[2.2.2]VL** was achieved to recover pure 3-cyclohexenecarboxylic acid as a monomer for condensation polymerization or precursor of another type of bicyclic lactone.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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